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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

004900-194

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.51)

**09/744686**INTERNATIONAL APPLICATION NO.  
PCT/FR99/01805INTERNATIONAL FILING DATE  
22 July 1999PRIORITY DATE CLAIMED  
29 July 1998

TITLE OF INVENTION

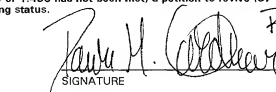
**MIXED MASKED (POLY)ISOCYANATES**

APPLICANT(S) FOR DO/EO/US

**Eugenie CHARRIERE; Jean-Marie BERNARD**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
  2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
  3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and the PCT Articles 22 and 39(1).
  4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
  5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
    - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
    - b. ☒ has been transmitted by the International Bureau.
    - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
    - ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
    - ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
      - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
      - b. ☐ have been transmitted by the International Bureau.
      - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
      - d. ☐ have not been made and will not be made.
  6. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
  7. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
  8. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:**
11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  13. ☒ A **FIRST** preliminary amendment.
 ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
  14. ☐ A substitute specification.
  15. ☐ A change of power of attorney and/or address letter.
  16. ☐ Other items or information:

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.50) <b>09/744686</b>		INTERNATIONAL APPLICATION NO. PCT/FR99/01805		ATTORNEY'S DOCKET NUMBER 004900-194	
17. <input checked="" type="checkbox"/> The following fees are submitted:				<b>CALCULATIONS</b>	
<b>Basic National Fee (37 CFR 1.492(a)(1)-(5)):</b>				PTO USE ONLY	
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO . . . . . \$1,000.00 (960)					
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO . . . . . \$860.00 (970)					
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . . \$710.00 (958)					
International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . \$690.00 (956)					
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . \$100.00 (962)					
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>\$ 860.00</b>	
Surcharge of <b>\$130.00 (154)</b> for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)).				20 <input type="checkbox"/> 30 <input type="checkbox"/> \$	
Claims	Number Filed	Number Extra	Rate		
Total Claims	20 -20 =	0	X\$18.00 (966)	\$	--
Independent Claims	2 -3 =	0	X\$80.00 (964)	\$	--
Multiple dependent claim(s) (if applicable)				+ \$270.00 (968)	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$ 860.00</b>	
Reduction for 1/2 for filing by small entity, if applicable (see below).				\$ -	
<b>SUBTOTAL =</b>				<b>\$ 860.00</b>	
Processing fee of <b>\$130.00 (156)</b> for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492(f)).				20 <input type="checkbox"/> 30 <input type="checkbox"/> \$	
<b>TOTAL NATIONAL FEE =</b>				<b>\$ 860.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by appropriate cover sheet (37 CFR 3.28, 3.31). <b>\$40.00 (581)</b> per property +				\$	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$ 860.00</b>	
				Amount to be: refunded \$	
				charged \$	
<p>a. <input type="checkbox"/> Small entity status is hereby claimed.</p> <p>b. <input checked="" type="checkbox"/> A check in the amount of \$ <u>860.00</u> to cover the above fees is enclosed.</p> <p>c. <input type="checkbox"/> Please charge my Deposit Account No. <u>02-4800</u> in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>d. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>02-4800</u>. A duplicate copy of this sheet is enclosed.</p> <p><b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b></p> <p>SEND ALL CORRESPONDENCE TO:</p> <p>Norman H. Stepno BURNS, DOANE, SWECKER &amp; MATHIS, L.L.P. P.O. Box 1404 Alexandria, Virginia 22313-1404 (703) 836-6620</p> <div style="text-align: right; margin-top: 20px;">         SIGNATURE  <hr/>       Norman H. Stepno        NAME  <hr/> <u>30,427</u>        REGISTRATION NUMBER     </div>					

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JC07 Rec'd PCT/PTO

29 JAN 2001

Attorney's Docket No. 004900-194

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of )  
Eugenie CHARRIERE et al. ) Group Art Unit: Unassigned  
Application No.: Unassigned ) Examiner: Unassigned  
(Corresponds to PCT/FR99/01805) )  
International Filing Date: 22 July 1999 )  
For: MIXED MASKED )  
(POLY)ISOCYANATES )

PRELIMINARY AMENDMENT

BOX PCT

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination, please amend the above-captioned application as follows:

IN THE CLAIMS:

Kindly cancel claims 1-19, without prejudice or disclaimer and insert the following claims in lieu thereof:

--20. A composition comprising isocyanates, at least partially blocked by at least two different blocking agents, one of the blocking agents reacting with the isocyanate functional group via an OH group and the other reacting with the isocyanate functional group via an NH group or the two blocking agents reacting with the isocyanate functional group via an OH group, the two blocking agents having a deblocking temperature of between 80 and 200°C in the octanol test and being selected so that, in the octanol test at 110°C, the ratio

percentage in equivalents of blocking agent which deblocks first at 110°C

D = \_\_\_\_\_  
percentage in equivalents of blocking agent which deblocks last at 110°C

is greater than 4/3, with the proviso that, when a blocking agent comprises a phenol functional group as blocking functional group, it does not comprise a COOH functional group and that, when the polyisocyanate composition comprises more than two blocking groups and one of the agents represents a five-membered nitrogenous heterocycle, the composition comprises more than 30 equivalent % of blocking agents reacting with the isocyanate functional group via the OH functional group.

21. A composition comprising isocyanates at least partially blocked, by at least two different blocking agents as defined in claim 20, wherein said ratio D is greater than 1.5.

22. A composition comprising isocyanates at least partially blocked by at least two different blocking agents as defined in claim 20, wherein said ratio D is greater than 2.

23. The composition of claim 20, wherein the ratio of the blocking groups is between 10/90 and 90/10.

24. The composition of claim 20, wherein one of the blocking agents is a substituted or unsubstituted (poly)nitrogenous heterocyclic compound.
25. The composition of claim 20, wherein the ratio of the blocking groups is between 20/80 and 80/20.
26. The composition of claim 20, wherein one of the blocking agents is selected from the group consisting of pyrazole, triazole and pyridine, optionally substituted.
27. The composition of claim 26, wherein one of the blocking agents is triazole, optionally substituted.
28. The composition of claim 20, wherein one of the two blocking agents is an oxime.
29. The composition of claim 20, wherein one of the blocking agents is an oxime selected from the group consisting of methyl ethyl ketoxime, acetone oxime, methyl amyl ketoxime, the oxime of methyl pyruvate and the oxime of ethyl pyruvate.
30. The composition of claim 20, wherein said blocking agents are selected from the pairs:
- triazole/methyl ethyl ketoxime,

- triazole/oxime of ethyl pyruvate,
- dimethylpyrazole/methyl amyl ketoxime,
- hydroxypyridine/methyl amyl ketoxime, and
- dimethylpyrazole/hydroxypyridine.

31. The composition of claim 20, comprising a mixture of compounds bearing blocked isocyanate functional group(s), wherein said compounds exhibit a mean functionality (number of blocked or nonblocked isocyanate functional groups per molecule comprising them) of greater than 2, and at most equal to 5.

32. The composition of claim 20, comprising a mixture of compounds bearing blocked isocyanate functional group(s), wherein said compounds exhibit a mean functionality (number of blocked or nonblocked isocyanate functional groups per molecule comprising them) at least equal to 2.1, and at most equal to 4.

33. The composition of claim 20, comprising a mixture of compounds bearing blocked isocyanate functional group(s) wherein said compounds exhibit a mean functionality (number of blocked or nonblocked isocyanate functional group per molecule comprising them) at least equal to 2.4.

34. The composition of claim 20, comprising a mixture of compounds bearing blocked isocyanate functional group(s) wherein said compounds exhibit a mean

functionality (number of blocked or nonblocked isocyanate functional group per molecule comprising them) at most equal to 3.7.

35. The composition of claim 20, comprising a mixture of compounds bearing blocked isocyanate functional group(s), wherein compounds bearing isocyanate functional groups fulfill at least one of the following conditions:

- at least one third of the free or blocked NCO functional groups are connected to a hydrocarbonaceous backbone via a saturated ( $sp^3$ ) carbon;
- at least one third of said saturated ( $sp^3$ ) carbons carry at least one ;
- at least one third of said saturated ( $sp^3$ ) carbons are connected to said backbone via a carbon atom itself bearing at least one hydrogen.

36. A kit for the preparation of a coating, comprising, for successive or simultaneous addition, a composition of claim 20 and a coreactant comprising a reactive hydrogen.

37. The kit of claim 30, for the preparation of a paint.

38. A process for the preparation of a composition, comprising the step of reacting a (poly)isocyanate composition, successively or simultaneously, with at least two different blocking agents, one of the blocking agents reacting with the isocyanate functional group via an OH group and the other reacting with the isocyanate functional group via an

NH group or the two blocking agents reacting with the isocyanate functional group via an OH group, the two blocking agents having a deblocking temperature of between 80 and 200°C in the octanol test and being selected so that, in the octanol test at 110°C, the ratio

percentage in equivalents of blocking agent which deblocks first at 110°C

D= \_\_\_\_\_

percentage in equivalents of blocking agent which deblocks last at 110°C

is greater than 4/3, with the proviso that, when a blocking agent comprises a phenol functional group as blocking functional group, it does not comprise a COOH functional group and that, when the polyisocyanate composition comprises more than two blocking groups and one of the agents represents a five-membered nitrogenous heterocycle, the composition comprises more than 30 equivalent % of blocking agents reacting with the isocyanate functional group via the OH functional group.

39. A process for the preparation of coating polymers, comprising the following steps:

- bringing together the composition of claim 20 and a coreactant which comprises derivatives exhibiting reactive hydrogens; and
- heating the reaction mixture thus formed to a temperature which allows crosslinking of the isocyanate groups of compounds with said coreactant.--



**REMARKS**

Entry of the foregoing amendment(s) is respectfully requested.

The claims have been amended to eliminate multiple dependency and to place them in better condition for U.S. patent practice.

Should the Examiner have any questions concerning the subject application, a telephone call to the undersigned would be appreciated.

Respectfully submitted,

BURNS, DOANE, SWECKER & MATHIS, L.L.P.

By: 

Teresa Stanek Rea  
Registration No. 30,427

Reg. No.  
24,116

P.O. Box 1404  
Alexandria, Virginia 22313-1404  
(703) 836-6620

Date: January 29, 2001

Mixed blocked (poly)isocyanates

The present invention relates to blocked (poly)isocyanate compounds and to their use in the manufacture of coatings.

More specifically, the present invention relates to (poly)isocyanates, some at least of the isocyanate functional groups of which are blocked or protected by at least two thermolabile protective radicals, which radicals are sometimes identified by the term "blocking" or "blocking".

A particular subject matter of the present invention is molecular compounds constituting a unit, whether mono-, oligo- or polymeric in nature, which carries isocyanate groups and which can react with appropriate coreactants, such as alcohols, phenols, amines, aminophenols or aminoalcohols, advantageously at least partially bi- or polyfunctional coreactants, which can be mono-, oligo- or polymeric in nature.

The present invention also relates to a process for producing these new blocked polyisocyanates.

It additionally targets the use of the above blocked polyisocyanates in compositions for the preparation of polymers, especially of polycondensates and of reticulates resulting from the reaction of said protected polyisocyanates and of nucleophilic coreactants. This preparation is that which is used in industrial applications, such as coatings of all types and especially those on textiles, on glasses, on papers, on metals and on construction materials, and paints.

The usefulness of blocking isocyanate functional groups (blocking sometimes denoted by blocking), indeed even the necessity thereof, is explained by an excessively high reactivity at ambient temperature of isocyanates with respect to some coreactants or with respect to a reactive solvent, or to a generally continuous support phase in the case of emulsions or suspensions, such as water. This high

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reactivity is often highly restricting, especially for certain applications of polyurethanes, in particular in paints, because it makes it essential to separately package, and sometimes to separately handle, the isocyanate comonomer, resulting in a use which is not very convenient.

Thus, in all the applications of polyurethanes as coatings, it is of the greatest advantage to have available blocked isocyanates, in which the isocyanate functional group is rendered unreactive at ambient temperature with respect to its coreactants but maintained reactive at a higher temperature.

These blocked isocyanate units are advantageous in several respects. In the first place, they make it possible to provide, in one and the same packaging, coating compositions (including emulsions and suspensions) in which the isocyanate component is stable and relatively insensitive to water. It follows that it is no longer necessary to use expensive anhydrous solvents which are specific to isocyanates and that it is possible to store the blocked isocyanates for a long time, without deterioration, under conditions where those which are free would deteriorate.

The use of blocked polyisocyanates also makes it possible to reduce, indeed even to eliminate, the possible toxic risk associated with the presence of free and unstable isocyanates.

The improvement in this technique for blocking isocyanate functional groups on reactive mono-, oligo- or polymer units involves the optimization, in general a lowering, of the reaction temperature, that is to say that at which the deprotection is carried out, thus leading to the targeted polymerization and/or crosslinking.

More specifically, the deblocking temperature must be sufficiently high for there to be no risk of reaction during the storage period and this reaction

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temperature must be sufficiently low for it to be easy to carry out the polycondensation when this is desired.

In general, the "release" temperature of isocyanates, especially aliphatic isocyanates (that is to say that the carbon carrying the nitrogen has  $sp^3$  hybridization), is excessively high. Which implies that the goal is a lowering of this release temperature.

Such a lowering is reflected by not insignificant economic savings in energy and in process time.

Incidentally, it should be pointed out that the blocking groups used in the case of aromatic isocyanates cannot generally be used directly for aliphatic isocyanates, the "release" temperature for the same blocking group being several tens of degrees centigrade higher than that of the aromatic isocyanates.

Many blocking radicals have already been used. Mention may be made among them of, inter alia, triazoles, imidazolines, lactams, hydroxynitrogenous compounds, sodium bisulfites, isocyanate dimers, phenols, acetoacetic acid esters and alcohols. One of the most widely used groups is the group of dialkyl ketoximes, which, however, exhibits the major disadvantage of exhibiting a release temperature which is too high for many applications.

Among these blocking agents, only those with a deblocking temperature of between approximately  $80^{\circ}\text{C}$  (two significant figure) and  $200^{\circ}\text{C}$  (two significant figures) are regarded as true blocking agents, in other words those which respond positively to the octanol test within the temperature range from  $80^{\circ}\text{C}$  to  $200^{\circ}\text{C}$ .

It should be noted that the multiplicity of the parameters makes it difficult to systematize certain families.

Thus, one of the essential objectives of the present invention is to provide new polyisocyanates comprising blocked functional groups having a relatively low dissociation temperature for a limited

duration and with a dissociation yield compatible with polymerization techniques.

5 A second objective of the invention is to provide polyisocyanates comprising blocked functional groups which are soluble in the usual solvents used for this type of application.

Another objective of the invention is to provide new polyisocyanates comprising blocked functional groups which have little or no toxicity.

10 Another objective of the invention is to provide novel polyisocyanates comprising blocked functional groups which are not dangerous and/or problematic to handle and to use.

15 Another objective of the invention is to provide new polyisocyanates comprising blocked functional groups which are economical.

20 Another objective of the invention is to provide new polyisocyanates comprising blocked functional groups which give access to optionally crosslinked polymers (or rather to polycondensates) which satisfy the requirements of the applications.

In reality, these objectives are somewhat contradictory.

25 Thus, it is known that polyisocyanates comprising blocking functional groups of (poly)-nitrogenous heterocycle type, in particular triazole type, respond particularly well to the first objective of the invention but very poorly to the second because of their poor solubility in the usual solvents.

30 In addition, the use of these compounds is particularly advantageous because of their low cost.

Conversely, blocking groups of oxime type result in blocked polyisocyanates which exhibit good solubility in the usual solvents but which release the blocking group at higher temperatures. In addition, some free oximes are said to be toxic.

35 By virtue of the studies carried out by the inventors, it has been shown that some at least of these different objectives can be reconciled by

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blocking the polyisocyanates by means of two different blocking groups exhibiting a difference in reactivity and thus a difference in release temperature.

In particular, it has been shown that, when a composition comprising (poly)isocyanate(s) is at least partially blocked by two different blocking groups corresponding to the definition below, the overall release temperature, as measured by the octanol test explained in detail below, is that or at the very least very close to that of the group which is released in first place, that is to say the lowest temperature.

The various objectives set out above can be more advantageously reconciled when use is made of two different blocking agents exhibiting a difference in release temperature, one comprising a reactive hydrogen group -OH and the second a reactive hydrogen group -NH, respectively forming, by reaction with the NCO isocyanate functional groups, bonds of pseudourethane and urea type.

In an unpublished patent application, the Applicant Company has disclosed mixed blocked isocyanates which can be used in powder paints in which the isocyanate functional groups are blocked by at least two blocking agents, at least one of which exhibits a non-carbonaceous carboxyl functional group. In these isocyanates, however, the blocking role of the group carrying the carboxyl group is inseparable from the catalytic role.

The subject matter of the invention is thus an at least partially blocked composition comprising isocyanates, characterized in that it is blocked by at least two different blocking agents selected so that, in the octanol test at 110°C, the ratio

$$D = \frac{\text{percentage in equivalents of blocking agent which deblocks first at 110°C}}{\text{percentage in equivalents of blocking agent which deblocks last at 110°C}}$$

is greater than  $4/3$ , advantageously greater than 1.5, preferably greater than 2, with the proviso that, when a blocking agent comprises a phenol functional group as blocking functional group, it does not comprise a COOH functional group.

The deblocking percentages are measured at 110°C according to the octanol test on the isocyanate completely blocked by a single blocking agent, that for which the measurement is carried out.

The most commonly used blocking agents are those cited by M. Wicks in his article "Blocked isocyanates", Progress in Organic Coatings (1975), Vol. 3, p. 73; their deblocking temperatures are advantageously greater than 90°C.

The blocking agents can be divided into three groups:

- those for which the mobile hydrogen is carried by a chalcogen;
- those for which the mobile hydrogen is carried by a nitrogen;
- those for which the mobile hydrogen is carried by a carbon.

Among those for which the mobile hydrogen is carried by a chalcogen (preferably a light chalcogen, namely sulfur and oxygen), use is especially made of those where the chalcogen is an oxygen. Mention may in particular be made, among the latter, of:

- products comprising an >N-OH sequence, such as, for example, oximes (=N-OH) or hydroxyimides ( $[-CO-]_2N-OH$ ); and
- phenols, in particular those for which the aromatic nucleus is depleted in electrons, such as hydroxyphenols and hydroxybenzoates (for example, EP-A-680 984 and WO 98/4608).

Mention may also be made of the compounds disclosed in application EP-A-661 278.

Mention may in particular be made, among those for which the mobile hydrogen is carried by a nitrogen, of:

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- monosubstituted amides and in particular lactams (the most widely used being caprolactam);

- imides ( $[-CO-]_2N-H$ ), in particular cyclic imides, such as succinimide;

5       - unsaturated nitrogenous heterocycles, in particular with five ring members (advantageously doubly unsaturated), preferably comprising at least two hetero atoms (preferably nitrogen). Mention may be made, among the latter, of diazoles (such as  
10 glyoxalines and pyrazoles), triazoles or indeed even tetrazoles.

Mention may also be made of the compounds disclosed in application EP-A-661 278.

15       Mention may essentially be made, among those for which the mobile hydrogen is carried by a carbon, of compounds of malonic nature, that is to say an  $RCH<$  radical carrying two electron-withdrawing groups (such as carbonyl, nitrile, Rf or perfluoroalkyl).

20       Mention may therefore in particular be made of the following pairs of blocking agents: methyl amyl ketoxime/2-hydroxypyridine and dimethylpyrazole/2-hydroxypyridine.

25       To the knowledge of the Applicant Company, none of the pairs disclosed previously possesses either the advantages or the characteristic mentioned above. In particular, the pyrazole/triazole pair exhibits a ratio D of between 1.1 and 1.2.

30       A particular subject matter of the invention is an at least partially blocked composition comprising isocyanates, characterized in that it is blocked by at least two different blocking agents corresponding to the above condition, at least one of which reacts with the isocyanate functional group via an -OH group and at least another of which reacts with the isocyanate  
35 functional group via an -NH group.

Another subject matter of the invention is an at least partially blocked composition comprising isocyanates, characterized in that it is blocked by two (indeed even more) different blocking agents

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corresponding to the above condition which react with the isocyanate functional group via the -NH group.

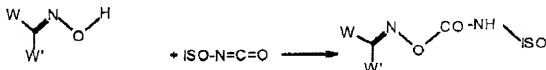
Mention may in particular be made of blocking agents of pyrazole or substituted pyrazole type.

- 5 Another subject matter of the invention is an at least partially blocked composition comprising isocyanates, characterized in that it is blocked by two different blocking agents corresponding to the above condition which react with the isocyanate functional  
10 group via the -OH group.

The two blocking groups are advantageously present in a ratio (expressed in equivalents of blocking functional group) of between 10/90 and 90/10, preferably 20/80 - 80/20.

- 15 Among the blocking compounds with a mobile hydrogen group carried by an OH group, oximes are preferred. Mention may in particular be made of methyl ethyl ketoxime, acetone oxime, methyl amyl ketoxime, the oxime of methyl pyruvate or the oxime of ethyl  
20 pyruvate (also denoted by "POME").

It should be remembered that oximes add to isocyanate functional groups, the hydrogen going to the nitrogen while the oxygen is grafted onto the carbon of the carbonyl, according to the scheme:



- 25 W and W', which are identical or different, representing aliphatic, alicyclic or aromatic hydrocarbonaceous or heterocyclic groups, it also being possible for W and W' together to represent a  
30 carbonaceous or heterocyclic ring. It is desirable for W and W' not to be simultaneously aromatic (that is to say that an aromatic ring is bonded directly to the carbon of the oxime functional group).

- 35 The W and W' groups can also comprise any type of substituent.

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Mention may be made, as examples of substituents, of alkyl, alkenyl, alkynyl, cycloalkyl, aryl, aralkyl, alkaryl, heterocyclic, alkoxy, perhaloalkyl (CF<sub>3</sub>, CCl<sub>3</sub> and the like) and polyalkoxy groups. The substituents can in particular be electron-withdrawing substituents, as disclosed in patent application WO 97/24386.

All substituents are suitable with the exception of those exhibiting a greater reactivity than the OH functional group of the oxime with the isocyanate functional group of the isocyanate compound.

The alkyl, alkenyl, alkynyl and alkoxy groups generally comprise from 1 (two for the alkenyl and alkynyl groups) to ten carbon atoms, preferably from 1 (two for the alkenyl and alkynyl groups) to six carbon atoms, the aryl groups advantageously being C<sub>6</sub>-C<sub>18</sub> aryl groups.

ISO represents the residue of the isocyanate molecule, which can comprise, as is described previously, (an) other isocyanate group(s).

Mention may in particular be made, among the blocking compounds with a mobile hydrogen carried by an >NH group, of nitrogenous heterocycles, in particular polynitrogenous heterocycles, preferably with five or six ring members, a few examples of which are composed of imidazole, pyrazole, triazoles (1,2,3-(triazole and 1,2,4-triazole), tetrazole and their substituted derivatives, triazoles being preferred.

The derivatives of these compounds carrying one or more substituents, that is to say at least one, two or three substituents, are also suitable, the substituents being as defined above for the oxime.

All the substituents are suitable, with the exception of those exhibiting a greater reactivity than the NH functional group of the nitrogenous heterocycle with the isocyanate functional group of the isocyanate compound.

These blocking groups of nitrogenous heterocycle type add to the isocyanate functional

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groups, the hydrogen going to the nitrogen while the nitrogen is drafted onto the carbon of the carbonyl of the isocyanate functional group, according to the scheme:



ISO being as defined above.

The preferred isocyanate compositions according to the invention are the compositions in which the blocking groups are respectively an oxime and triazole (1,2,3-triazole or 1,2,4-triazole), the oxime advantageously being methyl ethyl ketoxime, methyl amyl ketoxime, the oxime of methyl pyruvate or the oxime of ethyl pyruvate.

Surprisingly, it has been found that, when the polyisocyanate composition comprises triazole/oxime blocking groups, in particular for "true" oximes, that is to say oximes carrying two alkyl chains  $\alpha$  to the C carrying the N-OH group, in the abovementioned ratio (at least 10% and up to 90% of triazole groups, more particularly when it comprises at least 50% of triazole groups), the release temperature for the blocking groups is always less than that of the oxime group and close to that of the triazole group.

Triazole is a blocking agent which is very difficult to use because the compounds which it gives are only soluble in very few solvents. An additional advantage of the present invention is that of providing blocked compounds, one of the blocking agents of which is triazole (one mixed blocked compounds, one of the blocking agents of which is triazole (one or the other isomer, generally a mixture of the two), which have good solubility in the usual solvents while having the same advantages as triazole.

Consequently, in order to obtain good solubility, when one of the blocking agents is triazole, it is desirable for the latter to be combined with at least one blocking agent where the mobile hydrogen is carried by an oxygen, advantageously an

oxime. A triazole/all the blocking agents ratio by mass is advantageously at most equal to 2/3, preferably to 50%.

Problems of solubility are encountered when use is made, as blocking agents, of two different compounds exhibiting 5-membered nitrogenous heterocycles, in which case, in order to avoid crystallinity and thus insolubility in the solvents, it is desirable:

- either to have at least 1/3 of blocking groups comprising an -OH functional group;

- or to have blocking agents comprising 5-membered nitrogenous heterocycles carrying substituents, the sum in equivalents of the carbon atoms of the substituent groups with regard to the nitrogenous rings (number of carbon atoms of the substituent groups/number of 5-membered nitrogenous rings) being at least equal to 4, preferably to 6.

Generally, it is preferable for there to be not more than two blocking groups present in the composition.

However, when more than two blocking groups are present, it is preferable, in the case where the third group deblocks at a temperature in the vicinity of the deblocking temperature of the first, for the amount of blocking groups in addition to the two main groups not to exceed 30% in equivalents, advantageously not more than 25%, preferably not more than 20% and in particular not more than 15% in equivalents with respect to the sum of the blocked functional groups of the polyisocyanate composition.

As was mentioned above, the isocyanates for which the invention is most advantageous are those for which the nitrogen atom is bonded to a carbon with  $sp^3$  hybridization and more particularly aliphatic isocyanates. Mention may in particular be made of polymethylene diisocyanates (for example, TMDI (TetraMethylene Diisocyanate) and HDI [Hexamethylene Diisocyanate =  $OCN-(CH_2)_6-NCO$ ]) and their various condensation derivatives (biuret, and the like) and

"trimerization" derivatives (in the field under consideration, the mixtures resulting from the formation of isocyanuric rings from three isocyanate functional groups are known as trimer; in fact, there are, in addition to the true trimer, heavier products resulting from the trimerization).

Mention may also be made of isophorone diisocyanate (IPDI), norbornane diisocyanate (NBDI), 1,3-bis(isocyanatomethyl)cyclohexane (BIC), H<sub>12</sub>-MDI and cyclohexyl 1,4-diisocyanate.

Mention may also be made of arylenedialkylene diisocyanates, such as OCN-CH<sub>2</sub>-Ø-CH<sub>2</sub>-NCO.

It is desirable, in the structure of the monomer isocyanate(s), for the portion of the backbone connecting two isocyanate functional groups to comprise at least one polymethylene linkage (CH<sub>2</sub>)<sub>π</sub>, where π represents an integer from two to 10, advantageously from 4 to 8. This preference affects the mechanical performance. When there are several linkages, the latter can be alike or different. In addition, it is desirable for at least one, preferably all, these linkages to be free to rotate and thus exocyclic.

In addition it is preferable, in the blocked polyisocyanate composition, for reasons of crystallinity, for at least 20% of the monomer units of the (poly)condensation product to exhibit a polymethylene linkage (CH<sub>2</sub>)<sub>π</sub> as specified above.

When the polyisocyanate composition comprises more than two blocking groups, it is preferable, when one of the agents represents a 5-membered nitrogenous heterocycle, for more than 30 equivalent % of blocking agent(s) comprising an -OH reactive functional group to be present.

Generally, it is preferable to avoid the use of a blocking agent comprising a secondary amine group carrying two aliphatic chains, such as, for example, diisopropylamine.

Blocking agents comprising a nitrogenous heterocycle of aromatic or pseudoaromatic nature, such

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as pyrazole, triazole, imidazole, tetrazole, pyrazoline, and the like, and generally exhibiting an unsaturation in the ring, do not come within this category.

5 For the usual uses of isocyanates which are said to be completely blocked, the percentage of residual free isocyanate functional group is preferably at most equal to 5%, advantageously 2%, preferably 1%. The degree of release is quantified by the octanol test  
10 (see below).

According to the present invention, the blocked polyisocyanate, pure or as a mixture, results from a polyisocyanate, that is to say having at least two  
15 isocyanate functional groups, advantageously more than two (possibilities of fractional values since it is generally a mixture of more or less condensed oligomers), which itself generally results from a precondensation or from a prepolymerization of a diisocyanate unit (sometimes described in the present  
20 description as "monomer").

Generally, 90% of the molecules constituting the mixture of these prepolymers or of these precondensates before blocking have an average  
molecular mass at most equal to approximately 2 000  
25 (Mw), more commonly to approximately 1 000 (Mw), the term approximately meaning that the positional zeros are not significant figures (in other words, the single figure is significant in this case).

Thus, mention may be made, among the  
30 polyisocyanates used for the invention, of those of the biuret type and those which, by a di- or trimerization reaction, have resulted in four-, five- or six-membered rings. Mention may be made, among the six-membered rings, of the isocyanuric rings resulting from a homo-  
35 or from a heterotrimerization of various diisocyanates alone, with other isocyanate(s) [mono-, di- or polyisocyanate(s)] or with carbon dioxide gas; in this case, a nitrogen of the isocyanuric ring is replaced by

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an oxygen. Oligomers comprising isocyanuric rings are preferred.

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The preferred polyisocyanates are those which exhibit at least one aliphatic isocyanate functional group. In other words, at least one blocked isocyanate functional group according to the invention is connected to the backbone via a carbon of  $sp^3$  type advantageously carrying a hydrogen atom, preferably two hydrogen atoms. It is desirable for said carbon of  $sp^3$  type to be itself carried by a carbon of  $sp^3$  type advantageously equipped with one, preferably with two, hydrogen atoms, in order to avoid the isocyanate functional group under consideration from being in the neopentyl position. In other words, it is advisable to select, as monomers (which generally carry two isocyanate functional groups), at least one compound which carries at least one aliphatic functional group which is neither secondary or tertiary nor neopentyl.

When the composition according to the invention comprises a mixture of isocyanates, it is generally preferable for said mixture to exhibit a mean functionality (number of blocked or nonblocked isocyanate functional groups per molecule comprising them) of greater than 2, advantageously at least equal to 2.1, and at most equal to approximately 15, advantageously to 7, preferably at least equal to 2.4 and at most equal to 4.

The present invention can also be used for lattices and in particular lattices exhibiting blocked isocyanate functional groups such as disclosed in the European patents of the Applicant Company EP-A-739 961 and EP-A-674 667.

In addition, preference is given to the mixtures of isocyanate compounds in which at least one, advantageously at least two, preferably at least three, of the following conditions are combined:

- at least one third, advantageously two thirds, preferably four fifth, of the free or blocked NCO functional groups are connected to a

hydrocarbonaceous backbone via a saturated ( $sp^3$ ) carbon;

- at least one third, advantageously two thirds, preferably four fifth, of said saturated ( $sp^3$ ) carbons carry at least one, advantageously two, hydrogen(s);

- at least a third, advantageously at least a half, preferably at least two thirds, of said saturated ( $sp^3$ ) carbons are connected to said backbone via a carbon atom itself carrying at least one hydrogen, advantageously two.

The blocked polyisocyanates of the invention are obtained by reacting the polyisocyanates as defined above with the two types of blocking compounds, in particular a blocking compound comprising a reactive hydrogen contributed by an OH functional group and a blocking compound comprising a reactive hydrogen contributed by an NH functional group, successively or simultaneously.

One of the numerous advantages of the new polyisocyanates according to the invention is that they can act as base in the preparation of polymers and/or of crosslinked materials and can be used in particular as one of the main constituents of coatings of all types, such as varnishes and paints. In such uses, the qualities of hardness of the crosslinkable polymers are among those which are sought after at a technical and functional level.

The process for the preparation of polymers comprises the following stages:

- bringing together a blocked polyisocyanate according to the invention and a coreactant which comprises derivatives exhibiting reactive hydrogens in the form of alcohol, of phenol, of thiol or of certain amines, including anilines; these derivatives can have aliphatic, alicyclic or aromatic hydrocarbonaceous backbones, preferably alkyl backbones, including cycloalkyl and aralkyl or aryl backbones, which are linear or branched and substituted or unsubstituted

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(these coreactants, generally polyols, are known per se);

- and heating the reaction mixture thus formed to a temperature which makes possible crosslinking of the components.

Advantageously, the temperature is at most equal to approximately 300°C, preferably between 60 and 250°C and more preferably still between 100 and 200°C, for a duration of less than or equal to 15 hours, preferably of less than or equal to 10 hours and more preferably still of less than or equal to 8 hours.

It is possible to provide for the inclusion of an organic solvent in the reaction mixture. It is also possible to provide a suspension in water.

This optional solvent is preferably not very polar, that is to say the dielectric constant of which is scarcely greater than or equal to 4 or more preferably greater than or equal to 5.

In accordance with the invention, the preferred solvents which are not very polar are those which are well known to a person skilled in the art and in particular aromatic solvents, such as benzene, ketones, such as cyclohexanone, methyl ethyl ketone and acetone, light alkyl esters and in particular adipic esters, or petroleum fractions of the type of those sold under the trade name Solvesso®.

The derivatives forming part of the composition of the coreactant are generally di-, oligo- or polyfunctional, can be monomers or can result from di-, oligo- or polymerization, and are employed in the preparation of optionally crosslinked polyurethanes; their selection will be dictated by the functionalities expected for the polymer in the final application and by their reactivity.

In particular when it is desired to have stable "two-component" compositions (that is to say, simultaneously comprising the two reactants: the isocyanate, here at least partially blocked according to the invention, and the compound comprising reactive

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hydrogen), it is preferable to avoid the use of derivatives exhibiting reactive hydrogens which catalyze the release of the blocked isocyanate. Thus, among amines, it is preferable to use only those which  
5 do not catalyze the decomposition or the transamidation of the blocked isocyanate functional groups according to the present invention.

These coreactants are generally well known to a person skilled in the art.

10 The invention thus also relates to paint compositions comprising, for successive or simultaneous addition:

- a blocked polyisocyanate according to the invention;
- 15 - a coreactant comprising reactive hydrogen as described above;
  - possible catalysts known per se (in particular those based on tin for the oximes);
  - optionally at least one pigment;
  - 20 - optionally titanium dioxide;
  - optionally an aqueous phase;
  - optionally a surface-active agent for maintaining as an emulsion or for keeping in suspension the constituent components of the mixture;
  - 25 - optionally an organic solvent;
  - optionally a dehydrating agent.

The invention also relates to the paint and varnishes obtained by the use of these compositions, with the optional release according to the above  
30 process.

#### OCTANOL TEST

This is the test which defines the percentage of deblocking at a given temperature, which makes  
35 possible classification of the blocking agents.

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### definitions

"Release" (or : this is the lowest temperature at  
"deblocking") which the blocking agent of the  
temperature blocked isocyanate is 9/10  
(mathematically rounded off)  
displaced by a primary monoalcohol  
(the primary alcohol is generally  
octanol).

Shelf life : In order to ensure a good shelf  
life, it is preferable to choose  
blocked isocyanate functional  
groups for which the octanol test  
shows a "release" at 80°C,  
advantageously at 90°C, at most  
equal to 90%.

Progress of the : The reaction is considered to be  
reaction complete if it is carried out to  
more than 90%.

- 5 In the context of the present invention, the  
test is carried out at 110°C.

### procedure

- 10 Approximately 5 mmol of protected blocked NCO  
equivalent to be evaluated are charged to a Schott-type  
tube with magnetic stirring.

- 2.5 to 3 ml of 1,2-dichlorobenzene (solvent)  
equivalent of 1-octanol (5 mmol, i.e. 0.61 g, and  
optionally with the catalyst to be tested with the  
15 blocking group) are added.

- The reaction mixture is subsequently brought to  
the test temperature. Heating is then carried out for  
6 h at the test temperature, so as to deblock and thus  
render reactive the isocyanate functional groups. On  
20 completion of the reaction, the solvent is removed by  
vacuum distillation and the residue is analyzed by NMR,  
mass and infrared.

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The percentage of blocked isocyanate functional group condensed with the 1-octanol is evaluated from these data.

5 In the presence of a catalyst, the deblocking temperatures are lowered, with respect to the values shown, in proportion to the amount of catalyst introduced. The choice of the catalyst can also make it possible to vary the kinetics of deblocking of one of the blocking agents with respect to the other and  
10 consequently to vary the kinetics of crosslinking. The choice of the catalyst will be guided by the constraints of the desired application.

15 The following nonlimiting examples illustrate the invention.

Example 1

Preparation of HDT blocked with 50% MEKO/50% 1,2,4,-triazole.

500 g of HDT (true trimer of HDI), 68 g of MEKO  
20 and 53.9 g of 1,2,4-triazole in 140.6 g of AMP (propylene glycol monoethyl ether acetate) are introduced into a 500 ml jacketed reactor. An exothermic reaction takes place. At the end of the latter, the triazole is not completely dissolved.

25 The reaction mixture is heated with stirring at 80°C until the triazole has completely dissolved. After one hour at this temperature, 2.7 g of triazole are added and the operation is resumed one hour 30 later. The reaction is allowed to continue for a further one hour. 561.3 g of product are obtained, which product no longer comprises free NCO functional group and exhibits a potential NCO level of 11.56% and a viscosity at 25°C of 83.3 poises (8330 mPa.s).

35 D = 9.5

(% of deblocking at 110°C: MEKO: 2)

1,2,4-triazole:19)

- temperature for the deblocking of 90% of the blocked product: 150°C

Example 2:

5      **Preparation of HDT blocked with 25% MEKO/75% 1,2,4-triazole**

The reaction is carried out as for example 1, except that the following reactants are introduced:

HDT	: 300 g
1,2,4-triazole	: 85.8 g (5% excess)
MEKO	: 36 g (5% excess)
in AMP	: 140.6 g

10      The title product is obtained, which product no longer comprises free NCO functional groups and exhibits a potential NOC level of 11.8%.

D = 9.5

- temperature for the deblocking of 90% of the blocked product: 148°C

15      This product rapidly crystallizes, which reduces the advantage thereof for the envisage applications.

Example 3:

20      **Preparation of HDT blocked with 50% 1,2,4-triazole/50% POME**

The reaction is carried out as for example 1, except that the following reactants are introduced:

HDT	: 259 g
1,2,4-triazole	: 49.4 g (5% excess)
POME	: 93.7 g (5% excess)
in AMP	: 134 g

25      The title product is obtained, which product exhibits a few traces of free NCO functional group, a potential NCO level of 10.7% and a viscosity of 72 poises (7200 mPa.s).

D = 2.47

(% of deblocking at 110°C: POME=47)

30      - temperature for the deblocking of 90% of the blocked product: 145°C

Example 4:

Preparation of HDT blocked with 50% MEKO/50% 1,2,4-triazole in the absence of solvent.

5 The reaction is carried out as for example 1, except that the following reactants are introduced into the reactor:

HDT : 400 g  
1,2,4-triazole : 71.9 g  
MEKO : 92.1 g (1.5% excess)

A solid product is obtained, which product is crushed and stored in a freezer.

10 D = 9.5

Example 5:

Preparation of HDT blocked with 50% methyl amyl ketoxime/50% 3,5-dimethylpyrazole

15 The following reactant:

HDT : 250 g  
in Solvesso 100 : 133.1 g  
is introduced, while flushing with argon, into a 1 l round-bottomed flask equipped with a cooling system.

63.9 g of DMP are subsequently added via a funnel. The temperature changes from 20 to 45°C.

20 85.3 g of MAKO in a dropping funnel are subsequently added. The temperature changes from 45 to 62°C. The mixture is heated to 80°C and is maintained at this temperature for one hour. The title product is obtained, which product exhibits a potential NCO level  
25 of 10.43% and a viscosity of 22.1 poises (2210 mPa.s) at 25°C.

D = 7.5

- temperature for the deblocking of 90% of the blocked product: 152°C

30

Example 6:

Preparation of HDT blocked with 50% methyl amyl ketoxime/50% 2-hydroxypyridine

The following reactants:

HDT : 250 g  
2-hydroxypyridine : 64.8 g  
in Solvesso 100 : 133.4 g  
are introduced, while flushing with argon, into a 1 l  
round-bottomed flask equipped with a cooling system.

The mixture is heated to 80°C and is maintained  
5 at this temperature for one hour. It is cooled to 30°C.  
The following is added:

MAKO : 85.3 g

The mixture is heated at 80°C for one hour. The  
title product is obtained with a potential NCO level of  
10.4% and a viscosity at 25°C of 19.7 poises  
10 (1970 mPa.s).

D = 40

(% of deblocking at 110°C for 2-OHpyridine  
= 100)

- temperature for the deblocking of 90% of the  
15 blocked product: 145°C

Example 7:

Preparation of HDT blocked with 50% DMP/50%  
2-hydroxypyridine

20 The reaction is carried out as for example 6,  
except that DMP (64 g) is introduced in place of the  
MAKO and the amount of Solvesso 100 is 126.3 g.

The title product is obtained with a potential  
NCO level of 11.0% and a viscosity at 25°C of 30.7  
25 poises (3070 mPa.s).

D = 6.66

- temperature for the deblocking of 90% of the  
blocked product: 138°C

30 Example 8:

Preparation of HDT blocked with 80% MAKO/20%  
DMP

The following:

HDT : 250 g  
in Solvesso 100 : 137.7 g  
are introduced, while flushing with argon, into a 1 l  
round-bottomed flask equipped with a cooling system and  
with a system for regulating the temperature.

5 The following:

DMP : 26.6 g  
is added via a funnel and then the following:

MAKO : 136.5 g  
is added over 15 minutes via a dropping funnel.

The temperature rises from 20 to 73°C. The  
mixture is heated to 80°C and is maintained at this  
10 temperature for one hour.

The title product is obtained, which product  
exhibits a potential NCO level of 10.10% and a  
viscosity at 25°C of 17.8 poises (1780 mPa.s).

D = 6  
15 - temperature for the deblocking of 90% of the  
blocked product: 150°C

#### Example 9:

#### **Preparation of varnish**

20 Varnishes were prepared based on acrylic polyol  
(G-Cure 105P 70) with NCO/OH = 1.05 and 50% solids  
content (dilution solvent: EPP/Solvesso 100/RPDE:  
57/40/3) with three levels of catalysts:

- without DBTL (dibutyltin dilaurate)
- 25 - with 0.05% by weight of DBTL with respect to  
the dry varnish;
- with 0.5% by weight of DBTL with respect to  
the dry varnish.

The characteristics of the blocked isocyanates  
30 are as follows:

	1	2	3	4
HDI polyiso- cyanate	Trimer	Trimer	Trimer	Trimer
Blocking	MEKO	POME	MEKO/triazole	POME/triazole

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reactant			50/50	50/50
SC (%)	74	75	75	75
Solvent	Solvesso 100	Butyl acetate	AMP*	AMP*
NCO	11.20	9.80	11.56	10.70

\*AMP: propylene glycol monoethyl ether acetate

#### Applications

Each varnish was applied to glass plates (wet 200  $\mu$ m gauge), left desolvated for 30 minutes at ambient temperature and then stoved for 30 minutes at various temperatures from 110 to 160°C according to the amount of catalyst.

Twenty-four hours after stoving, the Persoz hardness and the resistance to MEK were measured. The combined analysis of these two measurements makes it possible to determine the deblocking (crosslinking) temperature for curing each of the varnishes for 30 minutes. The results are presented in the table below:

	without catalyst (°C)	with 0.05% DBTL (°C)	with 0.5% DBTL (°C)
1	160	150	140
2	140/150	130	120
3	150	140	130
4	140/150	130	120

Thus, it is seen to emerge that:

- for the same curing agent, the change from 0 to 0.05 and then 0.5% of DBTL decreases the blocking temperature by 10°C and 20°C respectively;

- the MEKO/triazole mixed blocking makes it possible to decrease the blocking temperature by 10°C at least with respect to MEKO alone, whatever the level of catalyst;

- the POME/triazole mixed blocking gives identical results to the POME alone blocking. This is consequently advantageous as regards cost.

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JC07 Rsc'd FC/10.0 29 JAN 2001

AMENDED CLAIMS

1. An at least partially blocked composition comprising isocyanates, characterized in that it is  
5 blocked by at least two different blocking agents, one of the blocking agents reacting with the isocyanate functional group via an OH group and the other reacting with the isocyanate functional group via an NH group or  
10 the two blocking agents reacting with the isocyanate functional group via an OH group, the two blocking agents having a deblocking temperature of between 80 and 200°C in the octanol test and being selected so that, in the octanol test at 110°C, the ratio

percentage in equivalents of blocking agent which deblocks first at 110°C

D= 
$$\frac{\text{percentage in equivalents of blocking agent which deblocks last at 110°C}}{\text{percentage in equivalents of blocking agent which deblocks first at 110°C}}$$

15 is greater than 4/3, advantageously greater than 1.5, preferably greater than 2, with the proviso that, when a blocking agent comprises a phenol functional group as blocking functional group, it does not comprise a COOH  
20 functional group and that, when the polyisocyanate composition comprises more than two blocking groups and one of the agents represents a five-membered nitrogenous heterocycle, the composition comprises more than 30 equivalent % of blocking agents reacting with  
25 the isocyanate functional group via the OH functional group.

2. Composition comprising isocyanates according to any one of the preceding claims, characterized in that the ratio of the blocking groups is between 10/90 and  
30 90/10, advantageously 20/80 and 80/20.

3. Composition comprising isocyanates according to any one of the preceding claims, characterized in that one of the blocking agents is a substituted or unsubstituted (poly)nitrogenous heterocyclic compound.

4. Composition comprising isocyanates according to claim 3, characterized in that the (poly)nitrogenous heterocyclic compound is selected from substituted or unsubstituted pyrazole, triazole and pyridine.

5 5. Composition comprising isocyanates according to claim 7, characterized in that the (poly)nitrogenous heterocyclic compound is substituted or unsubstituted triazole.

6. Composition comprising isocyanates according to any one of claims 1 to 5, characterized in that one of the two blocking agents is an oxime.

7. Composition according to claim 6, characterized in that the oxime is selected from methyl ethyl ketoxime, acetone oxime, methyl amyl ketoxime, the 15 oxime of methyl pyruvate and the oxime of ethyl pyruvate.

8. Composition according to claim 1, characterized in that the blocking agents are selected from the pairs:

- 20
- triazole/methyl ethyl ketoxime,
  - triazole/oxime of ethyl pyruvate,
  - dimethylpyrazole/methyl amyl ketoxime,
  - hydroxypyridine/methyl amyl ketoxime, and
  - dimethylpyrazole/hydroxypyridine.

25 9. Composition according to any one of the preceding claims comprising a mixture of compounds carrying blocked isocyanate functional group(s), characterized in that said mixture exhibits a mean functionality (number of blocked or nonblocked 30 isocyanate functional groups per molecule comprising them) of greater than 2, advantageously at least equal to 2.1, and at most equal to approximately 5, advantageously to 4.

10. Composition according to any one of claims 1 to 35 9, characterized in that said mixture exhibits a mean functionality (number of blocked or nonblocked isocyanate functional group per molecule comprising them) at least equal to 2.4.

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11. Composition according to any one of claims 1 to 10, characterized in that said mixture exhibits a mean functionality (number of blocked or nonblocked isocyanate functional group per molecule comprising them) at most equal to 3.7.

12. Composition according to any one of claims 1 to 11, in which the mixture of the compounds carrying isocyanate functional groups fulfills at least one, advantageously at least two, preferably at least three, of the following conditions:

- at least one third, advantageously two thirds, preferably four fifth, of the free or blocked NCO functional groups are connected to a hydrocarbonaceous backbone via a saturated ( $sp^3$ ) carbon;

- at least one third, advantageously two thirds, preferably four fifth, of said saturated ( $sp^3$ ) carbons carry at least one, advantageously two, hydrogen(s);

- at least a third, advantageously at least a half, preferably at least two thirds, of said saturated ( $sp^3$ ) carbons are connected to said backbone via a carbon atom itself carrying at least one hydrogen, advantageously two.

13. Composition according to any one of claims 1 to 12 for the preparation of a coating, characterized in that it additionally comprises, for successive or simultaneous addition, a coreactant comprising a reactive hydrogen.

14. Use of the compositions according to any one of claims 1 to 13 for the preparation of a coating, in particular a paint.

15. Process for the preparation of a composition according to any one of the preceding claims, characterized in that a (poly)isocyanate composition is reacted, successively or simultaneously, with the blocking agents as defined in one of claims 1 to 8.

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16. Process for the preparation of polymers, characterized in that it comprises the following stages:

- bringing together a blocked polyisocyanate as  
5 defined in any one of claims 1 to 13 and a coreactant which comprises derivatives exhibiting reactive hydrogens;

and

- heating the reaction mixture thus formed to a  
10 temperature which makes possible crosslinking of the components.

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# **COMBINED DECLARATION AND POWER OF ATTORNEY FOR UTILITY PATENT APPLICATION**

Attorney's Docket No.

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name:

I BELIEVE I AM THE ORIGINAL, FIRST AND SOLE INVENTOR (if only one name is listed below) OR AN ORIGINAL, FIRST AND JOINT INVENTOR (if more than one name is listed below) OF THE SUBJECT MATTER WHICH IS CLAIMED AND FOR WHICH A PATENT IS SOUGHT ON THE INVENTION ENTITLED:

" Mixed blocked (poly)isocyanates ".

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on July 22, 1999 as

Application No. PCT/FR9901805

and was amended on \_\_\_\_\_;  
(if applicable)

I HAVE REVIEWED AND UNDERSTAND THE CONTENTS OF THE ABOVE-IDENTIFIED SPECIFICATION, INCLUDING THE CLAIMS, AS AMENDED BY ANY AMENDMENT REFERRED TO ABOVE:

I ACKNOWLEDGE THE DUTY TO DISCLOSE TO THE OFFICE ALL INFORMATION KNOWN TO ME TO BE MATERIAL TO PATENTABILITY AS DEFINED IN TITLE 37, CODE OF FEDERAL REGULATIONS, Sec. 1.56 (as amended effective March 16, 1992);

I do not know and do not believe the said invention was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to said application; that said invention was not in public use or on sale in the United States of America more than one year prior to said application; that said invention has not been patented or made the subject of an inventor's certificate issued before the date of said application in any country foreign to the United States of America on any application filed by me or my legal representatives or assigns more than twelve months prior to said application;

I hereby claim foreign priority benefits under Title 35, United States Code Sec. 119 and/or Sec. 365 of any foreign application(s) for patent or inventor's certificate as indicated below and have also identified below any foreign application for patent or inventor's certificate on this invention having a filing date before that of the application(s) on which priority is claimed:

<b>COMBINED DECLARATION AND POWER OF ATTORNEY</b>	Attorney's Docket No.
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COUNTRY/INTERNATIONAL	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED
FRANCE	9809718	29/07/98	YES <input checked="" type="checkbox"/> NO <input type="checkbox"/>
			YES <input type="checkbox"/> NO <input type="checkbox"/>

I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:

William L. Mathis 17,337  
Robert S. Swecker 19,885  
Platon N. Mandros 22,124  
Benton S. Duffett, Jr. 22,030  
Norman H. Stepno 24,716  
Ronald L. Grudziecki 24,970  
Frederick G. Michaud, Jr. 25,003  
Alan E. Kopecki 25,813  
Regis E. Slum 26,999  
Samuel C. Müller, III 27,360  
Robert G. Mukai 28,531  
George A. Hovanec, Jr. 28,223  
James A. LaBarre 28,632  
E. Joseph Gess 28,510

R. Danny Huntington 27,903  
Eric H. Weisblat 30,505  
James W. Peterson 26,057  
Teresa Stanek Rea 30,427  
Robert E. Krebs 25,885  
William C. Rowland 30,888  
T. Gene Dillahunty 25,323  
Patrick C. Keane 32,838  
B. Jefferson Boggs, Jr. 37,344  
William H. Benz 25,952  
Peter K. Skiff 31,917  
Richard J. McGrath 20,192  
Matthew L. Schneider 32,814  
Michael G. Savage 32,396

Gerald F. Swiss 30,113  
Charles F. Wieland III 33,096  
Bruce T. Wieder 33,815  
Todd R. Walters 34,080  
Ronni S. Jillions 31,979  
Harold R. Brown III 36,341  
Allan R. Baum 36,086  
Steven M. duBois 35,023  
Brinn P. O'Shaughnessy 37,747  
Kenneth B. Lefler 36,075  
Fred W. Hathaway 37,336



**21839**

and: Norman H. Stepno

Address all correspondence to:



**21839**

Norman H. Stepno, Esquire  
BURNS, DOANE, SWECKER & MATHIS, L.L.P.  
P.O. Box 1404  
Alexandria, Virginia 22313-1404

Address all telephone calls to: \_\_\_\_\_ at (703) 836-6620.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

FULL NAME OF SOLE OR FIRST INVENTOR <u>EUGENE CHARRIERE</u>		SIGNATURE <i>[Signature]</i>	DATE <u>January 15<sup>th</sup> 2001</u>
RESIDENCE <u>52, rue d'Inkermann 69000 LYON FRANCE</u>		CITIZENSHIP <u>FRX</u>	French
POST OFFICE ADDRESS <u>The same as above</u>			
FULL NAME OF SECOND JOINT INVENTOR, IF ANY <u>Jean-Marie BERNARD</u>		SIGNATURE <i>[Signature]</i>	DATE <u>January 15<sup>th</sup> 2001</u>
RESIDENCE <u>Route du Large Saint Laurent d'Agnay 69440 MORNANT FRANCE</u>		CITIZENSHIP <u>FRX</u>	French
POST OFFICE ADDRESS <u>The same as above</u>			